Electrophilic Bromination of 7-Norbornylidene-7′-Norbornane. The Observation of an Unusually Large Inverse Deuterium Kinetic Isotope Effect

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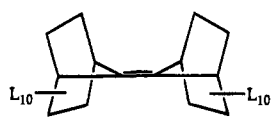
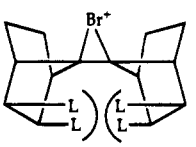
Abstract: The bromination of 7-norbornylidene-7′-norbornane (**1**) and its perdeuterated analogue (**2**) was studied in HOAc and MeOH by investigating the reaction kinetics and product distributions as a function of added [Br^-]. In all cases there is a significant inverse deuterium kinetic isotope effect on the bromination rate constant (k_g) which, in HOAc, is k_g(**2**/**1**) = 1.56 and 1.83 at [Br^-] = 0 and 0.04 M, respectively. Added Br^- causes a significant rate retardation which indicates the intervention of a reversibly formed bromonium ion intermediate. Product studies indicate the formation of four products, a normal dibromide and β-bromo solvate and two that arise from capture of an α-bromo cation formed from a Wagner–Meerwein rearrangement of the first-formed bromonium ion. In HOAc, added [Br^-] leads to an increase in the amount of the normal dibromide at the expense of the solvent-incorporated and rearranged products. In MeOH, dibromide is never an important product at any [Br^-] investigated, the two major isolated products being the normal methoxy bromide and rearranged ketone. Quantitative analyses of the products formed from bromination of **1** and **2** in HOAc as a function of [Br^-] indicate little difference in the product partitioning that is attributable to the presence of H or D. A unified mechanism that accommodates all the data is presented.

Introduction

Some time ago, Bartlett and Ho[1] reported that 7-norbornylidene-7′-norbornane (**1**) reacts slowly with Br_2 to give the corresponding 7,7′-dibromide. The slowness of the bromination must be attributable to severe steric crowding that restricts access to the backside of the intermediate bromonium ion. In earlier studies, we have observed that the perdeuterated molecule (**2**) exhibits a large inverse deuterium kinetic isotope effect (DKIE) relative to **1** for its reaction with Br_2 in HOAc or MeOH.[2] Application of DKIE's has proven valuable for studies of electrophilic bromination of olefins,[3-5] but the inverse nature of the deuterium isotope effect of **2**/**1** was unusual in that it appears to stem from a steric effect wherein the four inward facing (endo) C–L bonds are compressed in ion **3** and the transition states leading to and from it.[2] Herein we report the completed study of the bromination of **1** and **2** which includes detailed kinetic and product studies that show an unusual course for the reaction and the origins of the inverse DKIE.



1 L=H
2 L=D



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Experimental Section

A. Materials. 7-Norbornylidene-7′-norbornane (**1**) was prepared by a slight modification of the procedure of Bartlett and Ho.[1] 7-Norbornanone[6] (1.3 g, 11.8 mmol) was mixed with PBr_5[7] (10 g, 23.2 mmol), and the mixture was heated at 75 °C for 45 min after which it was poured into H_2O at 75–85 °C with stirring. The mixture was then extracted with 3 × 50 mL of CH_2Cl_2, and the combined extracts were washed with 30 mL of saturated $NaHCO_3$ and 2 × 30 mL of H_2O and then dried over $MgSO_4$. After filtration and rotary evaporation, the product was purified by chromatography (silica gel, petroleum ether) to give 2.0 g (67%) of 7,7-dibromonorbornane as a white solid having spectral data identical with those reported.[1] The dibromide was used immediately in the following coupling reaction.

To a mixture of Mg turnings (0.75 g, 35 mmol) and 5 mL of dry ether was added dropwise with stirring under Ar a solution of 0.905 g (3.5 mmol) of 7,7-dibromonorbornane in 4 mL of ether. An exothermic reaction began following the first few drops of the addition, which was continued at such a rate as to cause gentle reflux. After the addition, the reaction mixture was heated to reflux for 2 h after which it was filtered, and the filtrate volume increased by the addition of 20 mL more of ether. This solution was washed with H_2O and the aqueous wash extracted with 3 × 30 mL of ether. After drying over Na_2SO_4, removal of the solvent, and chromatography of the residue (silica gel, petroleum ether), 145 mg (37% crude) of a white solid was obtained which contained 15% of an unknown impurity. Final purification was effected by preparative gas chromatography (11 ft × 3/8 in. 20% DEGS on 80–100 mesh Chromosorb W, He flow 87 mL/min, T_1 = 180 °C for 5 min followed by a 2 °C/min rise to 195 °C). Spectral data were identical with those reported.[1]

7-Norbornylidene-7′-norbornane-d_{20} (**2**) was prepared by the route presented in Scheme 1. The deuterated dibromoethylene precursor was

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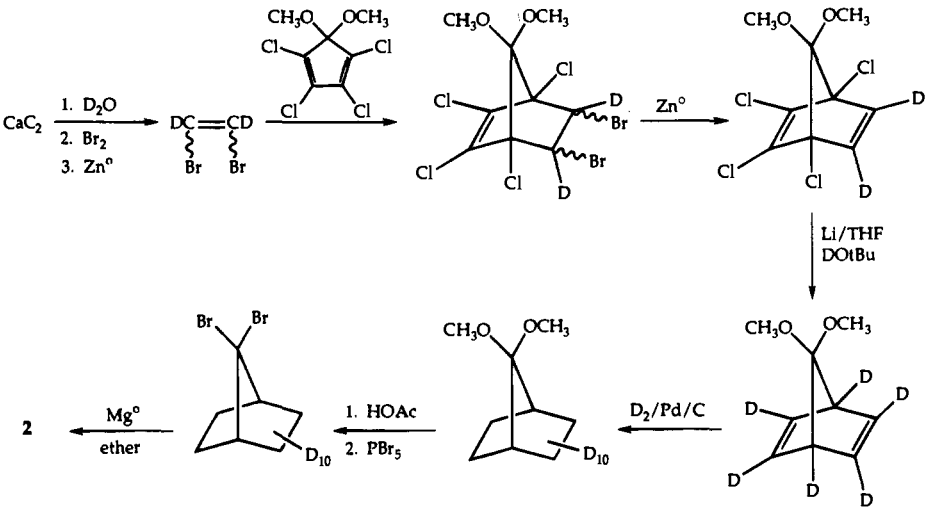
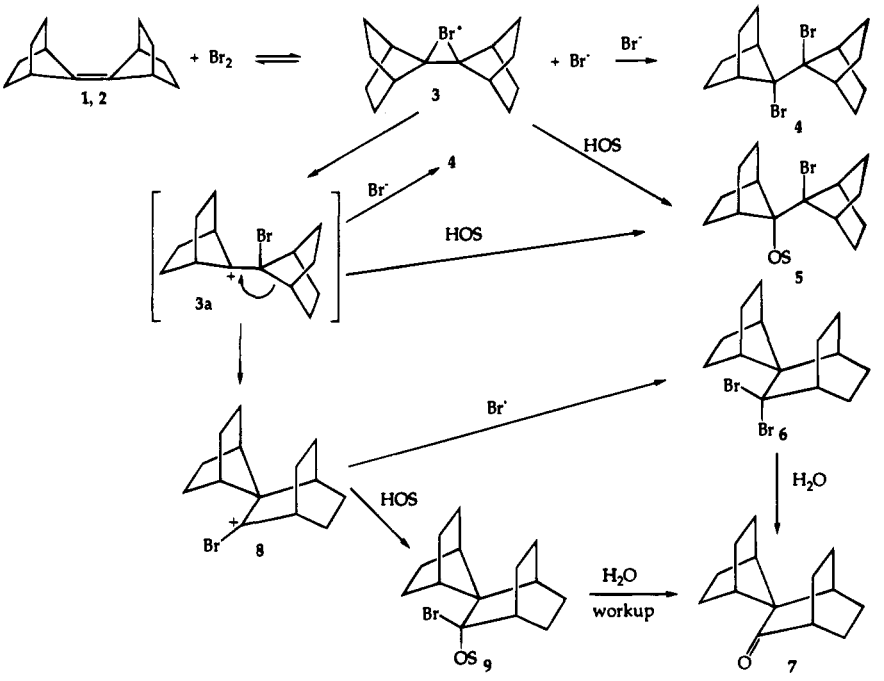
Scheme 1



Scheme 2. (HOS = $HOC(O)CH_3$, $HOCH_3$)



prepared by the method of LeBel et al.[8] and reacted with 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene to obtain 5,6-dibromo-1,2,3,4-tetrachloro-5,6-dideuterio-7,7-dimethoxybicyclo[2.2.1]hept-2-ene.[9] The synthesis was then carried on the perdeuterionorbornanone as described for the hydrogenated analogue[6] followed by coupling of the ketone via its dibromide and purification of the product as described above.

The ^1H content of **2** was determined by ^1H NMR in CD_2Cl_2 using a known amount of $CHCl_3$ as an internal standard. The signals at δ 2.40 (bridgehead), 1.47 (endo, syn to double bond), and 1.24 (exo, anti to double bond) showed 3%, 4.3%, and 7.2% protium, respectively.

B. Product Studies. The bromination of **1** in both HOAc and MeOH gives four products, two from normal addition and two that can be rationalized as arising from a Wagner–Meerwein rearrangement of the intermediate bromonium ion as in Scheme 2. These products were isolated from preparative scale reactions and identified by spectroscopic analysis as below.

Rearranged Ketone 7. Olefin **1** (10 mg, 5.3 mmol) was dissolved in 100 mL of dry HOAc and treated with a solution of 2 μL (9 mg) of Br_2 in 1 mL of HOAc. After the bromine color disappeared, 100 mL of CH_2Cl_2 was added and the mixture was extracted with 3 × 100 mL of H_2O, followed by 100 mL of saturated $NaHCO_3$ and more water washings until the washings were neutral. The organic phase was dried ($MgSO_4$) and then evaporated to give a residue that was crystallized from petroleum ether to give 4 mg of a white solid. Anal. C, H. ^1H NMR ($CDCl_3$): δ 2.18–2.05 (m, 4 H), 1.92–1.88 (apparent quintet, 1 H), 1.80–1.50 (m, 11 H), 1.21–1.12 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ 220.8, 65.4, 44.9, 42.1, 30.9, 30.0, 29.7, 23.8, 23.1. Ir (CH_2Cl_2 cast): 1721 cm^{-1}. Exact mass calcd for $C_{14}H_{20}$: 204.1514. Found: 204.1515.

Rearranged Dibromide 6. Olefin **1** (10 mg, 5.3 mmol) was dissolved in 10 mL of dry CCl_4 and 18 mg of Br_2 in 1 mL of CCl_4 added over a $^1/_2$ h period followed by allowing the mixture to stand in the dark for 24 h. The volatiles were then removed, and the residue was recrystallized from petroleum ether to yield 2 mg of white crystals that were of sufficient quality for X-ray diffraction, mp 144–145 °C. Anal. C, H. ^1H NMR ($CDCl_3$): δ 2.78–2.68 (m, 2 H), 2.64 (apparent quintet, J = 3 Hz, 1 H), 2.37–2.25 (m, 2 H), 2.10 (apparent quintet, J = 2 Hz, 2 H), 1.82–1.68 (m, 5 H), 1.65–1.51 (m, 2 H), 1.51–1.38 (m, 2 H), 1.37–1.25 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ 85.8, 66.5, 51.2, 46.4, 31.2, 31.0, 30.9, 25.4, 21.7. Exact mass calcd for $C_{14}H_{20}{}^{79}Br^{81}Br$: 347.9911. Found: 347.9912.

7′-(7-Bromo-7-norbornyl)-7′-methoxynorbornane (5, S = CH_3). To 10 mg (5.3 mmol) of olefin **1** in 100 mL of dry MeOH was added dropwise a solution of 9 mg of Br_2 in 1 mL of MeOH. After 30 min

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the volatiles were evaporated and the residue was recrystallized from petroleum ether to give 3 mg of white crystals that were of sufficient quality for X-ray diffraction. Anal. C, H. ^{1}H NMR ($CDCl_3$): δ 3.63 (s, 3 H), 2.83 (apparent t, J_{ap} = 4 Hz, 1 H), 2.61 (apparent t, J_{ap} = 4 Hz, 1 H), 2.38–2.25 (m, 2 H), 2.20–2.05 (m, 2 H), 2.05–2.0 (apparent t, J_{ap} = 4 Hz, 1 H), 2.0–1.66 (m, 5 H), 1.5–1.1 (m, 8 H). ^{13}C NMR ($CDCl_3$): δ 96.22, 91.48, 55.09, 48.45, 47.42, 46.44, 35.04, 33.16, 29.18, 29.09, 29.98, 28.74, 28.05, 26.23. Exact mass calcd for $C_{15}H_{23}O^{81}Br$, $C_{15}H_{23}O^{79}Br$: 300.0912, 298.0932. Found: 300.0914, 298.0931. Also peaks at 219.1749 (M^+ − Br), 187.1486 (M^+ − H, $BrOCH_3$), and 125.0966 ($C_8H_{13}O$).

7'-(7-Bromo-7-norbornyl)-7'-bromonorbornane (4). The solutions containing olefin **1** that were used for the determination of the bromination kinetics with added [Br^-] were combined and treated with the stoichiometric amount of Br_2 in HOAc and allowed to stand until bromination was complete. The mixture was then worked up by pouring it into 60 mL of H_2O which was then extracted with 3 × 20 mL of CH_2Cl_2. These combined extracts were washed with 1 × 50 mL of saturated Na_2CO_3 and 1 × 50 mL H_2O, after which the organic layer was dried over $MgSO_4$. Following filtration and rotary evaporation, the residue was chromatographed over silica gel using 75/25 CH_2Cl_2/hexane. The dibromide eluted first and was further purified by preparative TLC (SiO_2) using the same solvent system. ^{1}H NMR (300 μL $CHCl_3$ plus 35 drops of benzene): δ 3.6 (apparent t, J_{ap} = 4 Hz, 2 H), 2.99–2.85 (m, 2 H), 2.8–2.77 (apparent t, J_{ap} = 4 Hz, 2 H), 2.77–2.65 (m, 2 H), 2.5–2.39 (m, 2 H), 2.39–2.24 (m, 2 H), 2.02–1.92 (m, 2H), 1.91–1.78 (m, 4 H), 1.75–1.65 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ (91.57 (s), 55.19 (d), 47.70 (d), 35.67 (t), 28.99 (t), 28.95 (t), 27.90 (t). Exact mass calcd for $C_{14}H_{20}{}^{81}Br_2$, $C_{14}H_{20}{}^{79}Br^{81}Br$, $C_{14}H_{20}{}^{79}Br_2$: 349.9891, 347.9911, 345.9932. Found: 349.9887, 347.9894, 345.9929. Also peaks at 269.0727, 267.0747 (M^+ − Br), and 187.1487 ($C_{14}H_{19}$, 100%).

7'-(7-Acetoxy-7-norbornyl)-7'-bromonorbornane (5, S = C(O)-CH_3). This material, in our hands, could not be isolated in pure form because of its relative instability to H_2O and chromatographic separation. Its presence is clearly established from analyses of mixtures isolated as below.

To 50 mL of HOAc containing 0.1 M NaOAc and 10 mg of **1** was added dropwise 1 equiv of Br_2 in HOAc. The mixture was allowed to stand for 10 $t_{1/2}$ as determined from the kinetic studies (see below), after which it was poured into 20 mL of cold H_2O and quickly extracted with 3 × 20 mL of CH_2Cl_2. The extracts were combined and washed with H_2O and then saturated Na_2CO_3. Following drying ($MgSO_4$) of the mixture and removal of the volatiles, the residue was recrystallized as a mass from a small amount of CH_2Cl_2. This was analyzed by HPLC (see section D) as consisting of 25% of acetoxy bromide (**5**, S = C(O)-CH_3), 25% of the rearranged ketone **7**, and 50% of the dibromide **4**. By difference in the spectra of authentic **4** and **7** and those of the crystalline mass, **5** (S = $C(O)CH_3$) has the following spectral parameters. ^{13}C NMR ($CDCl_3$, −45 °C): δ 169.36, 100.10, 86.37, 48.97, 48.45, 47.69, 46.33, 34.94, 32.63, 28.77, 28.44, 28.35, 27.97, 26.19, 25.70, 21.82. ^{1}H NMR ($CDCl_3$): δ 2.06 (s, CH_3). GCMS (DB-5 column, T_1 = 40 °C, T_2 = 280 °C, at 20 °C/min): *m/z* 328.3, 326.3, (M^+), 247.2, 205.2, 153.1 ($C_7H_9OC(O)CH_3$). IR ($CDCl_3$ cast): 1744 cm^{-1}.

C. Kinetic Studies. The rates of bromination of **1** and **2** in purified HOAc (μ = 0.1 $LiClO_4$) or MeOH (μ = 0.3 $LiClO_4$) were determined at 25 °C under pseudo-first-order conditions of excess olefin and variable [LiBr] using Cary 210 or OLIS-17 spectrophotometers. Cuvettes (1 cm) containing 3.0 mL of solvent and ~1 × 10^{-3} M olefin were equilibrated at 25 °C in the spectrophotometer cell holder for 15 min, and then 100 μL of a stock Br_2 solution in the same solvent was added (final [Br_2] = 9 × 10^{-5} to 1 × 10^{-4} M). The kinetics were monitored by observing the rate of loss of absorbance at 410 nm. The absorbance vs time profiles were fit to a standard exponential model to yield pseudo-first-order rate constants (k_{obsd}). The second-order rate constants for the reactions were evaluated as $k_g = k_{obsd}$/[ol]. Reported in Tables 1 and 2 are the average k_g values (three to seven determinations) for bromination of **1** and **2** in both solvents.

D. Quantitative Product Studies. All the solutions that were used to determine the bromination kinetics at each [Br^-] in HOAc or MeOH were combined, and the stoichiometric amount of Br_2 (in HOAc or MeOH containing the identical [Br^-]) was added. The reaction mixtures were allowed to stand for the appropriate period of time to complete the reaction (> $10t_{1/2}$ as determined from kinetics) and then poured into 60 mL of H_2O. This was extracted with 3 × 20 mL of CH_2Cl_2, and the combined extracts were washed with aqueous Na_2CO_3 (50 mL) and H_2O (30 mL). Following drying ($MgSO_4$) of the solution and removal of the solvent, the residue was dissolved in 200 μL of CH_2Cl_2 and subjected to HPLC analysis: Hewlett Packard 1050 Series HPLC, RI detection, Waters RCM 8 × 10 C-18 reverse phase column, eluant 88/12 CH_3CN/H_2O, 1.5 mL/min for HOAc reactions, and 90/10 CH_3CN/H_2O, 2.0 mL/min for MeOH reactions. The retention times were 4.65 min for the rearranged ketone, 5.54 min for the acetoxy bromide, and 8.05 min for the 7,7'-dibromide in 88/12 CH_3CN/H_2O. For the methoxy bromide and ketone (**7**) in 90/10 CH_3CN/H_2O, 2.0 mL/min, the retention times were 5.87 and 3.36 min. Given in Table 3 are the percentages of the products from bromination of **1** and **2** in HOAc containing varying [Br^-]. In Table 4 are presented the products found for bromination of **1** in MeOH. The values given are the averages of at least three determinations and are estimated to have errors of ±3–5%.

E. Crystallography. Crystals of methoxybromide (**5**, S = CH_3) and rearranged dibromide (**6**) of sufficient quality for X-ray diffraction

Table 1. Second-Order Rate Constants for Bromination of **1** and **2** in HOAc Containing Varying [LiBr] at 25 °C, μ = 0.1 ($LiClO_4$)

[LiBr] (M)	k_g(**1**) (M^{-1} s^{-1})[a]	k_g(**2**) (M^{-1} s^{-1})[a]	k_g(**2/1**)[b]
0.0	37.6 ± 0.08	58.8 ± 3.2	1.56 ± 0.09
0.01	2.23 ± 0.12	3.68 ± 0.24	1.65 ± 0.14
0.02	0.90 ± 0.03	1.58 ± 0.07	1.76 ± 0.10
0.03	0.32 ± 0.05	0.66 ± 0.01	1.83 ± 0.08
0.04	0.30 ± 0.01	0.55 ± 0.01	1.83 ± 0.07

[a] $k_g = k_{obsd}$/[ol]; k_{obsd} is the pseudo-first-order rate constant for the disappearnce of Br_2 in the presence of excess [ol]; average of three to six determinations; quoted error is 1 standard deviation from the mean. [b] Error analyzed as $\delta z = |z|[(\delta x/x)^2 + (\delta y/y)^2]^{1/2}$, where x, y, and z are k_g(**1**), k_g(**2**), and k_g(**2/1**), respectively, and δx and δy are the standard deviationss in k_g(**1**) and k_g(**2**).

Table 2. Second-Order Rate Constants for Bromination of **1** and **2** in MeOH Containing Varying [LiBr] at 25 °C, μ = 0.3 ($LiClO_4$)

[LiBr] (M)	k_g(**1**) (M^{-1} s^{-1})[a]	k_g(**2**) (M^{-1} s^{-1})[a]	k_g(**2/1**)[b]
0.005	3.33 ± 0.6		
0.01	17.7 ± 0.4	33.2 ± 1.0	1.88 ± 0.07
0.02	6.24 ± 0.05	11.8 ± 0.6	1.89 ± 0.10
0.03	3.13 ± 0.15	5.98 ± 0.03	1.91 ± 0.09
0.04	1.85 ± 0.01	3.12 ± 0.06	1.69 ± 0.03

[a] $k_g = k_{obsd}$/[ol]; k_{obsd} is the pseudo-first-order rate consatnt for the disappearance of Br_2 in the presence of excess olefin; average of three to six determinations; quoted error is 1 standard deviation from the mean. [b] Error analyzed as $\delta z = |z|[(\delta x/x)^2 + (\delta y/y)^2]^{1/2}$, where x, y, and z are k_g(**1**), k_g(**2**), and k_g(**2/1**), respectively, and δx and δy are the standard deviations in k_g(**1**) and k_g(**2**).

Table 3. Percentages of Products Isolated from Bromination of **1** or **2** in HOAc as a Function of [LiBr], μ = 0.1 ($LiClO_4$)

		%product[b]		
olefin[a]	[LiBr] (M)	**4**	**5** (S = $C(O)CH_3$)	**6** + **7**[c]
1	0	5	25	70
2	0	2	32	66
1	0.01	13	23	64
2	0.01	13	26	61
1	0.02	22	21	57
2	0.02	22	25	53
1	0.03	25	19	55
2	0.03	27	22	51
1	0.04	34	17	49
2	0.04	35	20	45

[a] [olefin] ≃ 1 × 10^{-3} M; 1 equiv of Br_2 added in five equal portions. [b] Analyzed by HPLC: Waters RCM 8 × 10 C-18 column, eluent 88/12 CH_3CN/H_2O, flow = 1.5 mL/min, refractive index (R.I.) detection error estimated at ±3–5%. [c] Rearranged dibromide hydrolyzes to **7** during work-up procedure.

Table 4. Percentages of Products Isolated After Bromination of **1**[a] in MeOH at Varying [LiBr], μ = 0.1 ($LiClO_4$)

	%products[b]		
[LiBr] (M)	**4**	**5** (S = CH_3)	**6** + **7**[c]
0.0	n.o.	10	0 + 90
0.01	n.o.	20	2 + 78
0.03	0.4	30	5 + 65
0.05	0.6	38	9 + 53

[a] [olefin] ≃ 1 × 10^{-3} M; 1 equiv of Br_2 added in five equal portions. [b] Analyzed by HPLC: Waters RCM 8 × 10 C-18 column, eluent 90/10 CH_3CN/H_2O; flow 2.0 mL/min; R.I. detection, error estimated at ±3−5%. n.o. = not observed. [c] Rearranged dibromide hydrolyzes to ketone during workup; the percent of **6** is the lower limit of what is actually produced.

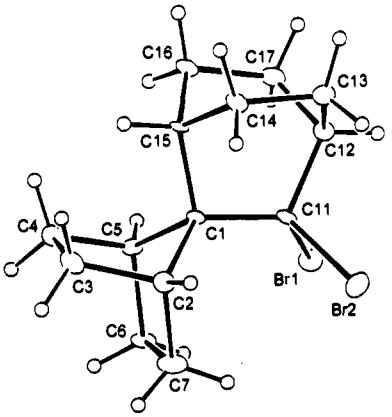


Figure 1. Ortep drawing of the methoxy bromide product **5** (S = CH_3). Elipsoids are given at the 20% probability level.

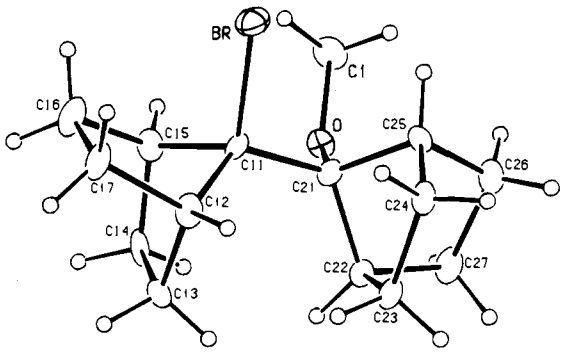


Figure 2. Ortep drawing of the rearranged dibromide product **7**. Elipsoids are given at the 20% probability level.

were obtained as described above. The ORTEP structures are shown in Figures 1 and 2. Complete crystallographic information is given as supporting information.

Results

A. Synthesis. Olefin **1**, in our hands, was best prepared by the method of Bartlett and Ho.[1] Its perdeuterated analogue **2** was prepared by the route given in Scheme 1by utilizing the reported procedure of Gassman and Pape[6] to 7-norbornanone except we started with deuterated precursors.[7-9] The key step in either synthesis is the coupling of 7-norbornanone which in our hands could be accomplished in only low and variable yields by McMurray coupling[10,11] despite several attempts with variations.[12] From the combined reaction residues of several of these attempts could be isolated olefin **1**, but the composite yield was 5%. The better procedure uses a slight modification of the Bartlett and Ho[4] route with careful chromatographic purification of 7,7-dibromonorbornane (silica gel, hexane) immediately followed by Mg coupling as described in the experimental procedure. The crude reaction product in this case consists of an 85/15 mixture of **1** and some other unknown impurity, this being separable by preparative GLPC as described in the Experimental Section.

B. Kinetics. Given in Tables 1 and 2 are the rate constants for disappearance of Br_2 under pseudo-first-order conditions of excess **1** and **2** and varying amounts of LiBr in HOAc or MeOH (μ = 0.1 and 0.3 ($LiClO_4$), respectively). Added Br^- causes a marked rate depression, so much so that at high [Br^-] in HOAc one must take precautions that competing (free radical?) reactions do not complicate the kinetics. Indeed, at [Br^-] = 0.05 M, the kinetics solutions retain some yellow color of uncertain origin at the completion of the reaction so that the kinetic constants determined at that concentration are considered unreliable.[2] From the data presented in Tables 1 and 2, one can discern two important points, namely that added [Br^-] markedly retards the reaction rate and that, for a given set of conditions, there is an inverse deuterium kinetic isotope effect, k_g(**2**/**1**) > 1. Of note also is the fact that, in HOAc, the DKIE appears to becoming progressively inverse as [Br^-] increases, reaching a plateau of ~1.8 ± 0.1 at 0.03−0.04 M. In MeOH, the inverse DKIE is independent of [Br^-], at least between 0.01 and 0.04 M, the k_g(**2**/**1**) being ~1.8 ± 0.1.

C. Reaction Products. Given in Tables 3 and 4 are the percentages of the various products isolated from the bromination reactions in HOAc or MeOH solvents at varying [Br^-]. The percentages are simply those based on the areas under the HPLC traces and are not corrected for the response factors of the various materials to refractive index detection. These corrections are probably small but are of little consequence to the analysis since we are mostly interested in the trends in product amounts as a function of [Br^-]. Quantitative analysis is made only for the comparison of the individual products from the hydrogenated and deuterated materials, for which a given product is assumed to have a response factor independent of the presence of H or D. Due to the instability of rearranged dibromide **6** to the work-up conditions, its relative percentage is only a lower limit of what is actually produced during the reaction. For the purposes of the analysis we designate that the sum of the amounts of ketone **7** and observed **6** is the true measure of the amount of material produced via the rearrangement. The point of note in MeOH is that the normal dibromide **4** is never an important product, the two major ones being rearranged materials (ketone **7**) and methoxy bromide **5**, (S = CH_3), the amount of which increases as [Br^-] increases.

In HOAc, where more detailed studies were conducted, there are two points to note. First, added [Br^-] causes a marked increase in dibromide **4** at the expense of both the acetoxy bromide (**5**, S = $C(O)CH_3$) and rearranged materials (**6** + **7**). Second, the product distribution obtained from bromination of the deuterated olefin (**2**) is very similar to that obtained from **1**, the only difference possibly being slightly more rearranged material and less **5** (S = $C(O)CH_3$) for the hydrogenated olefin relative to **2**. Given the errors of ±3−5% estimated for the HPLC analysis, the slight difference in the (**6** + **7**)/**5** ratios obtained from **1** and **2** may not be significant.

Discussion

The reaction of **1** and Br_2 in the two solvents we have investigated gives rise to four isolable products, the origins of

(10) Flemming, M. P.; McMurray, J. E. *Org. Synth.* **1981**, *60*, 113.
(11) Seymour, C. A. Ph.D. Dissertation, Massachusetts Institute of Technology, 1982. We thank Professor Frederick D. Greene of MIT for providing us with these experimental details.
(12) Marchand, A. P.; Reddy, G. M.; Deshpande, M. N.; Watson, W. H.; Nagl, A.; Lee, O. S.; Osawa, E. *J. Am. Chem. Soc.* **1990**, *112*, 3521.

which can be rationalized as in Scheme 2. Two of these can be explained as arising from Br^- or solvent (HOS) capture of the bromonium ion (**3**) or its open β-bromo carbocation (**3a**) and the others from capture of a Wagner–Meerwein rearranged α-bromocarbocation (**8**). An analogous process has been reported by Marchand and co-workers[12] for the bromination of *meso*-tris(homocubylidene-d_3)-tris(homocubane-d_3). In the present case, capture of the presumed α-bromo cation **8** by Br^- leads to the rearranged dibromide **6**, the structure of which was unambiguously proved by X-ray diffraction (Figure 1). While we have no definite proof, it is also possible that capture of **8** by solvent yields the α-bromo solvate **9**, which surely must undergo solvolysis under the aqueous work-up conditions to yield ketone **7**. Isolation of dibromide **6** is possible if the reaction products are isolated without aqueous workup, or if the workup/extraction is performed quickly. Indeed, the dibromide originally isolated[1] from the bromination of **1** in CCl_4/5% Br_2 had reported spectral parameters identical to those we have determined for **6** and quite different from those we have determined for authentic normal dibromide **4**. Control experiments in this work established that authentic **6** is readily converted into ketone **7** on exposure to H_2O. The same phenomenon was observed by Marchand and co-workers[12] for the rearranged gem dibromide formed during bromination of *meso*-tris(homocubylidene-d_3)-tris(homocubane-d_3).

Methoxy bromide **5** (S = CH_3), acetoxy bromide **5** (S = $C(O)CH_3$), and dibromide **4** proved somewhat difficult to analyze by ^1H or ^{13}C NMR because of the complex spectral patterns. Thus, the ^{13}C spectra indicated the presence of seven carbons for **4** and 14 for **5** (S = CH_3). This is expected if there is a significant barrier to rotation about the central C–C bond,[13] since if rotation were rapid the ^{13}C spectra would have four and nine signals, respectively.

Unambiguous proof for the structure of **5** (S = CH_3) was obtained by X-ray diffraction (Figure 2) which show an O–C–C–Br dihedral angle of 92.9 (8)°. Apparently the observation of 14 rather than the expected 15 signals in the ^{13}C spectrum of the latter is due to a degeneracy of two of the CH_2 signals. In the case of the acetoxy bromide, at ambient temperature, only broad signals were apparent, but at −45 °C, a total of 16 sharp signals attributable to that species was observed.

In a preliminary account of this work,[2] we reported that there were three observations of note for the bromination of **1** and **2**. These were that (a) added $[Br^-]$ causes a very prominent rate depression for the bromination in both MeOH and HOAc; (b) in both solvents, there is an inverse DKIE for the bromination (in HOAc the DKIE becomes increasingly inverse as $[Br^-]$ increases, but in MeOH, the DKIE is independent of $[Br^-]$ over the studied range 0.005–0.04 M); and (c) in HOAc, the amount of normal dibromide **4** increases at the expense of acetoxy bromide as $[Br^-]$ increases. In MeOH, dibromide **4** is never an important reaction product. Thus, it appeared that the increasingly inverse DKIE noted for **2/1** in HOAc as a function of $[Br^-]$ was tied to the production of dibromide **4**. Since the strong common ion rate depression indicates that product forming steps are rate limiting, it seemed reasonable that quantitative determination of the products of Br_2 addition to both **1** and **2** would allow one to sort out the origins of the DKIE.

We have confirmed the earlier observations in the current studies, but note that the reaction is more complicated than previously believed mainly because of the intervention of a competing molecular rearrangement of the bromonium ion **3** which yields dibromide **6** and after workup ketone **7**. Thus, in both solvents, as can be judged by the data in Tables 3 and 4, the rearrangement pathway is prominent at no added $[Br^-]$ and is progressively less so as the $[Br^-]$ increases. We will deal with all these observations in turn.

(a) **Kinetics.** It is well-established[14] that the rates of bromination of olefins generally decrease in the presence of $[Br^-]$. This is due to the instantaneous establishment of an equilibrium, $Br^- + Br_2 \rightleftharpoons Br_3^-$, the net effect being to decrease the available $[Br_2]_{free}$. In HOAc and MeOH, the equilibrium constants (K_{eq}) for this process are 92 and 177 M^{-1}, respectively.[14a,b] Both Br_2 and Br_3^- (or its kinetic equivalent[15])are brominating agents, and it can be shown[14] that the global second-order rate constant for disappearance of Br_2 is

$$k_g = (k_{Br_2} + k_{Br_3^-}K_{eq}[Br^-])/(1 + K_{eq}[Br^-]) \qquad (1)$$

where $k_g = k_{obsd}/[ol]$. For most normal olefins, a plot of $k_g(1 + K_{eq}[Br^-])$ vs $K_{eq}[Br^-]$ yields a straight line, the slope of which is $k_{Br_3^-}$, the rate constant for the tribromide reaction, the intercept being k_{Br_2}, the rate constant for the Br_2 reaction.

When the data for **1** and **2** in both solvents are manipulated in this way, the plots show marked downward curvature.[2] This sort of behavior has been reported in two previous cases, those of bromination of 2-acetoxy-2-cholestene[16] and tri-*tert*-butylethylene,[17] and was interpreted in terms of a marked Br^- promoted common ion rate depression. By analogy, the observations made for **1** and **2** can be explained, invoking the presence of a reversibly-formed bromonium ion (**3**) where the rate-limiting steps involve rearrangement and/or nucleophilic capture on C. Also consistent with this would be a process involving a reversibly formed bromonium ion (**3**) with subsequent slow opening to a β-bromo carbocation (**8a**) followed by rapid rearrangement/nucleophilic capture. MMX calculations[18] of the structure of ion **3** indicate that the C_2, C_2', C_3, and C_3' *endo* hydrogens are separated by only 2.11 Å, substantially less than the sum of their van der Waals radii (2 × 1.2 Å).[19] A similar crowding of the analogously positioned H's in the adamantylideneadamantane bromonium[20a] and iodonium[20a,b] ions is observed and must be the source of their stability toward nucleophilic capture on C. By reasonable analogy, steric crowding of the *endo* H's in **3** must be present in the transition states leading to and from that ion which accounts for the relatively slow bromination of **1** (**2**) and for the common ion

(13) MMX calculations indicate that the gauche form of **4** (Br–C–C–Br dihedral angle of 79.5°) is favored over the *syn* and *anti* forms by ~30.5 and 19.7 kcal/mol, respectively. For the methoxy bromide **5** (S = CH_3), the gauche form (Br–C–C–O dihedral angle of 92.2°) is also computed to be highly favored over its *syn* and *anti* forms in agreement with the X-ray structure. Calculated with the PCMODEL program V 5.1 (Serena Software, Box 3076, Bloomington, IN, 47402-3076).

(14) (a) Rolston, J. H.; Yates, K. *J. Am. Chem. Soc.* **1969**, *91*, 1477, 1483. (b) Dubois, J.E.; Hegarty, A. F.; Bergman, E. D. *J. Org. Chem.* **1972**, *37*, 2218. (c) Bartlett, P. D.; Tarbell, D. S. *J. Am. Chem. Soc.* **1936**, *58*, 466. (d) Dubois, J. E.; Huymh, X. Q. *Tetrahedron Lett.* **1971**, 3369 and references therein.

(15) (a) Bellucci, G.; Bianchini, R.; Ambrosetti, R.; Ingrosso, G. *J. Org. Chem.* **1985**, *50*, 3313. (b) Bellucci, G.; Bianchini, R.; Vecchani, S. *Ibid.* **1986**, *51*, 4224.

(16) Calvet, A.; Josefowicz, M.; Levisalles, J. *Tetrahedron* **1983**, *39*, 103.

(17) Dubois, J. E.; Loizos, M. C. *C. R. Seances Acad. Ser. C* **1972**, *274*, 1130.

(18) Calculated with the PC MODEL program (Serena Software, Box 3076, Bloomington, IN, 47402-3076). The Br^+–C force constants and parameters chosen for the calculation of bromonium ion **3** were chosen so as to duplicate the known geometry for the three-membered ring in the bromonium ion of adamantylideneadamantane.[20]

(19) Bondi, A. *J. Chem. Phys.* **1964**, *68*, 441.

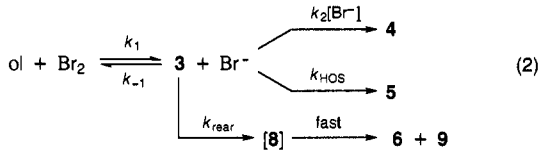
(20) (a) Ślebocka-Tilk, H.; Ball, R. G.; Brown, R. S. *J. Am. Chem. Soc.* **1985**, *107*, 4504. (b) Brown, R. S.; Nagorski, R. W.; Bennet, A. J.; McClung, R. E. D.; Aarts, G. H. M.; Klobukowski, M.; McDonald, R.; Santarsiero, B. D. *Ibid.* **1994**, *116*, 2448.

rate depression since added Br^- preferentially captures the ion on the exposed Br^+. In HOAc, the rate reduction produced by increasing $[Br^-]$ is so dramatic that, at $[Br^-] = 0.05$ M, the ionic addition is retarded to the point where competing, perhaps free radical, reactions occur, leading to the observation of other, as yet unidentified, products. For that reason, we have limited the data interpretation for that solvent to $0 < [Br^-] \leq 0.04$ M.

(b) Inverse DKIE. The large inverse DKIE observed for k_g (**2/1**) is unusual. Remote secondary DKIE's can arise from any or all of three possible effects, hyperconjugative, inductive, or steric,[21] and these possibilities in the case of **1** were previously discussed.[2] Inductive effects of 1−2% for replacement of each C−H bond in **1** with a slightly more dontating C−D bond in **2** cannot be ruled out with certainty,[22] but they cannot account for all of the inverse DKIE, nor can they explain the increasingly inverse DKIE as a function of added $[Br^-]$.

The most rational interpretation of the inverse DKIE involves a steric effect attributable to the strong compression of the *endo* C−L bonds in **3**. Because the amplitudes of vibration of C−D bonds are effectively less than those of C−H bonds,[21,23-25] the C−D bond appears somewhat shorter and less sterically demanding so that there will be less compression of the *endo* C−L bonds in the rate-limiting transition state for electrophilic addition to **2** than **1**. Accordingly, one anticipates that the deuterated material will react faster. In the simplest interpretation neglecting inductive contributions, the inverse DKIE can be apportioned equally to the four endo C−L bonds, with a DKIE of 1.12−1.16 per C−L bond. These values are at the high end of the range expected for steric DKIE's.[23-25]

(c) Quantitative Analysis of the DKIE. There are two plausible mechanisms that we consider likely for this process which account for the change in the DKIE observed at HOAc at increasing $[Br^-]$. Given in eq 2 is one simplified reaction



(2)

scheme for the bromination of **1** (**2**) involving a reversibly-formed bromonium ion (**3**) that partitions to addition products (**4** and **5**) in competition with an irreversible Wagner−Meerwein rearrangement leading to the α-bromo cation (**8**) which subsequently quickly is captured by Br^- or HOS (for structures see Scheme 2). Steady state (in **3**) analysis gives

$$k_g = k_{obsd}/[ol] = \frac{k_1(k_2[Br^-] + k_{HOS} + k_{rear})}{(k_{-1} + k_2)[Br^-] + k_{HOS} + k_{rear}} \quad (3)$$

At one limit, when $[Br^-] = 0$, there is no reversal or dibromide product being formed from *external* Br^-,[26] so we can simplify eq 3 as

$$k_g = \frac{k_1(k_{HOS} + k_{rear})}{(k_{HOS} + k_{rear})} = k_1 \quad (4)$$

Thus, with no added $[Br^-]$, the inverse DKIE of 1.56 in HOAc is related to

$$\frac{k_g^D}{k_g^H} = \frac{k_1^D}{k_1^H} \quad (5)$$

the kinetic isotope effect on the step leading to the bromonium ion **3** and is independent of the DKIE on all other steps.

In another limit, at high $[Br^-]$, the fact that one sees a strong common ion rate depression must mean that $k_{-1}[Br^-] > (k_2[Br^-] + k_{HOS} + k_{rear})$. In this limit, one simplifies eq 3 to

$$k_g = \frac{k_1}{k_{-1}[Br^-]}\left(1 + \frac{k_{HOS} + k_{rear}}{k_2[Br^-]}\right)k_2[Br^-] \quad (6)$$

and if $k_{-1}[Br^-]$ is sufficiently fast relative to the product forming steps, k_1/k_{-1} is approximated by an equilibrium constant, K, yielding

$$k_g = \frac{K}{[Br^-]}\left(1 + \frac{k_{HOS} + k_{rear}}{k_2[Br^-]}\right)k_2[Br^-] \quad (7)$$

Therefore, at high $[Br^-]$, the DKIE is given as

$$\frac{k_g^D}{k_g^H} = \frac{K^D}{K^H}\frac{\left(1 + \frac{k_{HOS} + k_{rear}}{k_2[Br^-]}\right)^D}{\left(1 + \frac{k_{HOS} + k_{rear}}{k_2[Br^-]}\right)^H}\frac{k_2^D}{k_2^H} \quad (8)$$

and is controlled by the isotope effect on four terms; these are the equilibrium constant for formation of **3** + Br^- from **1** (**2**) + Br_2 and the three product forming processes involving rearrangement of **3** and its capture by Br^- or HOAc. The quantitative determination of the products (Table 3) allows us to determine the effect of deuteration on $(k_{HOS} + k_{rear})/k_2[Br^-]$ and $k_2[Br^-]$ simply by comparing the percentages of the appropriate products arising from bromination of the hydrogenated and deuterated cases. This is accomplished as indicated below.

From eq 2 we can define the fraction of dibromide (**4**) product in terms of the various product-forming rate constants as

$$f_4 = \frac{k_2[Br^-]}{k_2[Br^-] + k_{HOS} + k_{rear}} \quad (9)$$

from which it follows that

(21) (a) Melander, L.; Saunders, W. H., Jr. *Reaction Rates of Isotopic Molecules*; Wiley Interscience: New York, 1980; pp 170, 181, 189. (b) *Isotope Effects in Chemical Reactions*; Collins, C. J., Bowman, N. S., Eds.; ACS Monograph 167; Van Nostrand Reinhold: New York, 1970; pp 56–63. (c) Bartell, L. S. *J. Am. Chem. Soc.* **1961**, *83*, 3567. (d) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987; pp 232–244. (e) Westaway, K. C. In *Isotopes in Organic Chemistry*; Buncel, E., Lee, C. C., Eds.; Elsevier: Amsterdam, 1987; Vol. 7, pp 275–392.

(22) In principle, it should be possible to ascertain the importance of inductive effects by stereospecifically synthesizing the d_8 olefin where the eight *endo* C−L bonds are deuterated.

(23) (a) Melander, L.; Canter, R. E. *Acta Chem. Scand.* **1964**, *18*, 1138. (b) *Idem. J. Am. Chem. Soc.* **1964**, *86*, 295. (c) Mislow, K.; Graeve, R.; Gordon, A. J.; Wahl, G. H., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 1733; **1963**, *85*, 1199. (d) Raaen, V. F.; Dunham, T. K.; Thompson, D. D.; Collins, C. J. *J. Am. Chem. Soc.* **1963**, *85*, 3497. (e) Carter, R. C.; Melander, L. *Adv. Phys. Org. Chem.* **1973**, *10*, 1. (f) Sherrod, S. A.; Boekelheide, V. *J. Am. Chem. Soc.* **1972**, *94*, 5513. (g) Sherrod, S. A.; da Costa, R. L.; Barnes, R. A.; Boekelheide, V. *J. Am. Chem. Soc.* **1974**, *96*, 1565. (h) Anet, F. A. L.; Basus, V. J.; Hewett, A. P. W.; Saunders, M. *J. Am. Chem. Soc.* **1980**, *102*, 3945.

(24) (a) Leffek, K. T.; Llewellyn, J. A.; Robertson, R. E. *Can. J. Chem.* **1960**, *38*, 1505, 2171; *J. Am. Chem. Soc.* **1960**, *82*, 6315. (b) Durand, R.; Geneste, P.; Lamaty, G.; Rogue, J. P. *Tetrahedron Lett.* **1977**, 199.

(25) Brown, H. C.; McDonald, G. J. *J. Am. Chem. Soc.* **1966**, *88*, 2514.

(26) Note that internal return from an intimate ion pair would not be detectable in this study but can be accommodated by a kinetically equivalent expression where $k_1 = K_{iip}k_1'$, where K_{iip} is the equilibrium constant between ol + Br_2 and the intimate bromonium ion/Br^- ion pair and k_1' is the separation rate constant for the iip into separated ions.

$$\frac{1}{f_4} = 1 + \frac{k_{HOS} + k_{rear}}{k_2}\frac{1}{[Br^-]} \quad (10)$$

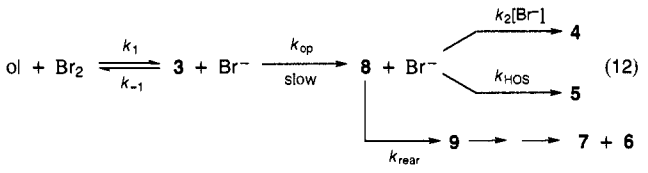
Thus, a plot of $1/f_4$ vs $1/[Br^-]$ should yield a straight line, the slope of which is $(k_{HOS} + k_{rear})/k_2$. Using the percentages of products given in Table 3, the slopes of the plots for the data for **1** and **2** are 0.082 ± 0.005 and 0.074 ± 0.004 M, respectively. *That these numbers are identical within experimental uncertainty suggests that there is no marked dependence of the product partitioning on the isotope composition of bromonium ion 3.* Furthermore, the data in Table 3 indicate that the relative amounts of dibromide **4** formed from **1** or **2** are identical at each $[Br^-]$ so there cannot be a preference for Br^- capture of the deuterated species relative to the hydrogenated one, e.g., $k_2^D[Br^-]/k_2^H[Br^-] = 1$. Hence, the product data indicate that at high $[Br^-]$ eq 8 can be simplified as

$$\frac{k_g^D}{k_g^H} = \frac{K^D}{K^H}\frac{\left(1 + \frac{0.074}{[Br^-]}\right)}{\left(1 + \frac{0.082}{[Br^-]}\right)} \simeq \frac{K^D}{K^H} \quad (11)$$

Thus, should the process depicted in eq 2 be operative, the change in the inverse DKIE is attributable to the $[Br^-]$ dependent shift from a *kinetic* isotope effect on k_1, to an equilibrium isotope effect on the formation of the bromonium ion.

An Alternative, More Probable, Analysis. If the reaction pathway proceeds as in eq 2 via a bromonium ion with subsequent rate-limiting partitoning to product, then it is surprising that there is no discernable isotopically sensitive discrimination of the $k_2[Br^-]$, k_{HOS}, or k_{rear} steps. Indeed, as previously indicated, the four *endo* H's in **3** are in such close contact that it is difficult to envisage how backside nucleophilic attack can occur at all unless the ion has somehow rearranged to allow access to a more open site. Clearly, increasing $[Br^-]$ leads to more of the normal dibromide and normal acetoxy bromide is also produced so the carbon framework of **1** must be intact at the point where such capture occurs. Importantly, the product data indicate that each of the dibromide (**4**), acetoxy bromide (**5**, S = C(O)CH$_3$), and rearranged materials arise from a common intermediate. This is evidenced by the fact that the $[Br^-]$-dependent formation of **4** does not alter the acetoxy bromide/rearranged ketone ratio (0.35−0.37 from data in Table 3, $[Br^-]$ = 0.01 M → 0.04 M).

Given in eq 12 is a scheme which also accounts for the data but is intuitively more satisfying because the product-forming steps occur by post-rate-limiting capture of a far less sterically encumbered β-bromo cation (**8** as in Scheme 2):



(12)

Steady state (in **3**) analysis gives

$$k_g = \frac{k_{obsd}}{[ol]} = \frac{k_1 k_{op}}{k_{-1}[Br^-] + k_{op}} \quad (13)$$

At zero added $[Br^-]$, eq 13 reduces to

$$k_g = k_1 \quad (14)$$

and the DKIE is as it was for the previous analysis:

$$\frac{k_g^D}{k_g^H} = \frac{k_1^D}{k_1^H} \quad (5)$$

At high $[Br^-]$, the marked common rate depression indicates that $k_{-1}[Br^-] > k_{op}$ so that eq 13 reduces to

$$k_g = \frac{k_1}{k_{-1}[Br^-]}k_{op} \quad (15)$$

Correspondingly, if formation of the bromonium ion + Br^- from ol + Br_2 can be considered a true equilibrium at high $[Br^-]$, then $k_1/k_{-1} = K$, and the DKIE is

$$\frac{k_g^D}{k_g^H} = \frac{K^D}{K^H}\frac{k_{op}^D}{k_{op}^H} \quad (16)$$

In this second analysis, as in the first, at low $[Br^-]$, the inverse DKIE depends exclusively upon the k_1 step, while at high $[Br^-]$, it depends upon an equilibrium effect and the kinetic step for opening of the bromonium ion to a β-bromo carbocation. Importantly, for either analysis, the kinetic DKIE and its increase as a function of $[Br^-]$ is not tied to any of the product-forming steps but rather depends exclusively upon the steps for formation and opening of **3**.

For either of the analyses we have presented, the fact that the DKIE increases and plateaus at high $[Br^-]$ can be qualitatively explained by considering that the transition state leading to bromonium ion **3** experiences less compression of the endo C−L bonds than does the bromonium ion itself. Thus it is reasonable that the DKIE would be less inverse if k_1 were the rate-limiting step and that the isotope effect on the equilibrium constant should be somewhat more inverse. In the case of our preferred mechanism of eq 12, it is difficult to say what the DKIE would be on the step where the bromonium ion opens to the β-bromo carbocation **8**, although one might anticipate k_{op}^D/k_{op}^H should be <1 if significant C−L compression were being relieved in its transition state.

(d) The Bromination in MeOH. Although we have not investigated it as extensively, the bromination of **1** and **2** in MeOH must occur by fundamentally the same mechanism as it does in AcOH. One observes an inverse DKIE on k_g (**2/1**) and products that arise from rearrangement and solvent capture on ions **3** or **8**. These are two observations that are somewhat different in MeOH. First, the DKIE is constant from 0.01 M < $[Br^-]$ < 0.04 M. Unfortunately, due to the rapidity of the reaction, we could not determine k_g (**2/1**) for the bromination in MeOH at $[Br^-]$ = 0 M, but it may be that, as is the case in HOAc, this value is slightly less than it is at high $[Br^-]$.

Second, the data in Table 4 show that increasing amounts of methoxy bromide (**5**, S = CH$_3$) are formed in the presence of increasing $[Br^-]$, but there is very little detectable dibromide (**4**) product even at the highest $[Br^-]$ used. This sort of behavior has been seen previously for bromonium ions[27] and S_N1-generated cations[28] wherein anionic nucleophiles are capable

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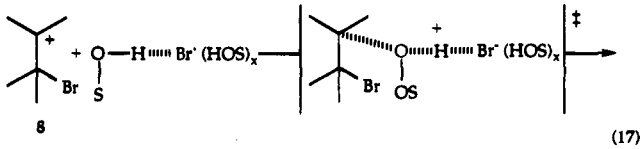
(28) (a) Goering, H. C.; Hopf, H. *J. Am. Chem. Soc.* **1971**, *93*, 1224. (b) Shiner, V. J., Jr.; Hartshorn, S. R.; Vogel, P. C. *J. Org. Chem.* **1973**, *38*, 3604. (c) Okamoto, K.; Kinoshita, T.; Oshida, T.; Yamamoto, T.; Ito, Y.; Dohi, M. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1617. (d) Okamoto, K.; Takeuchi, K.; Inoue, T. *Ibid.* **1980**, 842. (e) McManus, S. P.; Zutaut, S. E. *Tetrahedron Lett.* **1984**, *25*, 2859. (f) Allen, A. D.; Kanagasabapathy, V. M.; Tidwell, T. T. *J. Am. Chem. Soc.* **1985**, *107*, 5413. (g) Okamoto, K. *Adv. Carbocation Chem.* **1989**, *1*, 171.

of assisting in the delivery of a polarized solvent molecule, probably by collapse of a solvent-separated ion pair as in eq 17.[4,27]



8 (17)

Conclusions

In the above study, analysis of the products formed from bromination of the hydrogenated and deuterated alkene indicates virtually no isotopic sensitivity of the partitioning ratio. Thus the amount of dibromide product **4** formed from capture of the intermediate(s) increases in response to added Br^- in the medium, but this fact is not related to the increasingly inverse DKIE (k_g(**2**/**1**)). Rather, the latter is tied to the reversal of the bromonium ion intermediate, but only insofar as the DKIE changes from a kinetic one on bromonium ion formation at zero added [Br^-] to an equilibrium effect at high [Br^-]. The study serves to illustrate the importance of bromonium ion reversal in Br_2 addition to congested olefins and the importance of steric compression of the C−L bonds in the ion and transition states leading to it.

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Supporting Information Available: Complete X-ray crystallographic data for compounds **5** (S = CH_3) and **6** (28 pages); listings of structure factors for **5** (S = CH_3) and **6** (33 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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